EPA United States Environmental Protection Agency

Land Application Field Study II



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Outline

- Previous Research
- Experimental Design
- Data
  - Metals
  - Nonylphenol
  - PFAS
- Conclusions
- Next Steps
- Acknowledgements

Disclaimer

The views expressed in this presentation are those of the authors and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency.

Multimedia Land Application Study: Field Study I

- Surface application by side discharge manure spreader
- Agronomic rate of 10 wet tons/acre
- Material applied
  - Anaerobically digested biosolids
  - Polymer addition during dewatering
  - Lime addition
- Application field
  - Fescue field
  - No prior application of biosolids
  - Autumn application
  - Sampled for 1 month before and 4 months after application

Soil Study Activities

- Characterize Study Conditions
  - Weather data
  - Soil data
  - Quantity and distribution of biosolids
  - Microbial community quantity and structure
- Performance Measurements
  - Microbes: fecal coliform density, viable helminth ova, Salmonella, enteric viruses, coliphage
  - Chemicals: concentrations of alkylphenol ethoxylates and degradation products (APEs)
  - Ecotoxicity Screening

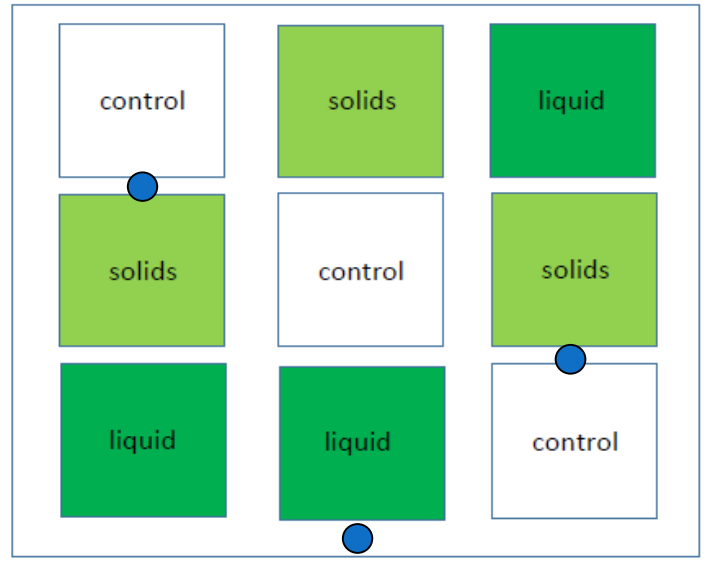
Soil Study Conclusions

- Changes observed in shallow samples after application
- Microbial community shifted for about 28 days after application
- Total biomass, fecal coliforms, and APEs
  - Increased following application
  - Persisted for 98 day sampling period

- See full results in report “Multimedia Sampling During the Application of Biosolids on a Land Test Site”
  - Report - https://www.epa.gov/sites/production/files/2018-11/documents/multimedia-sampling-land-testsite.pdf
  - Summary - https://www.epa.gov/sites/production/files/2018-11/documents/study-examines-fate-agricultural-land.pdf

Land Application Field Study II

- Research Questions
  - How does concentration change with time when biosolids are land applied?
  - Does the application method (Solid or Liquid) affect measured concentrations?
- Pilot/Field scale Treatment plot at local WWTP on a fescue and rye grass field
- Fall application at 10 wet tons/acre
- Study Design
  - Land application techniques (liquid and solids)*
  - No application (control) and biosolids only (blue circles)*
  - 3 Treatment reps of each
  - Sampled for 13 months*
- Analytes
  - Microbes: fecal coliforms, total biomass and community structure
  - Nutrients
  - Chemicals: metals, APEs, and PFAS*



* Changed from previous study

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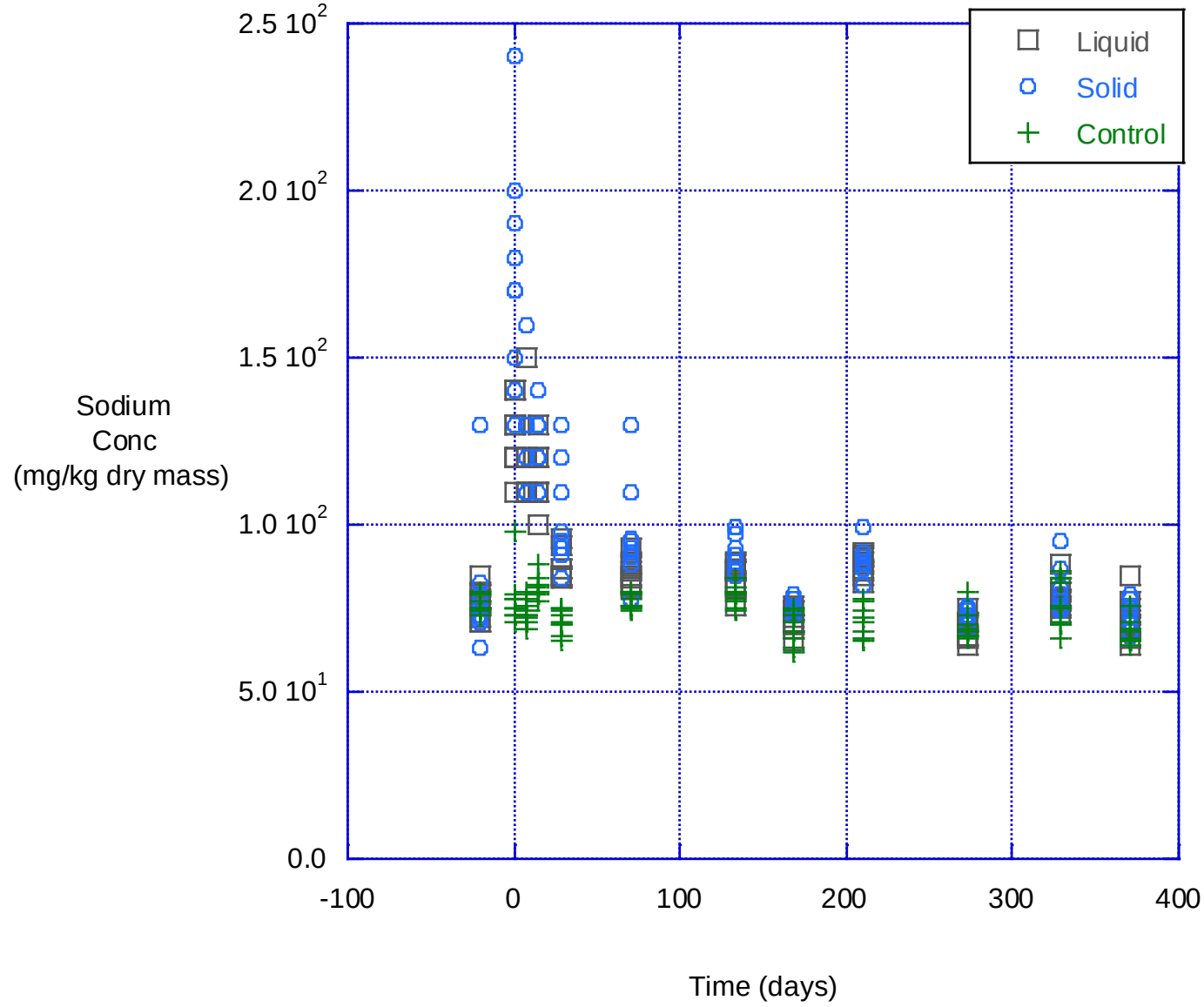
Samples from the Plots

Control **Solid** **Liquid**

Sodium Data

Concentrations

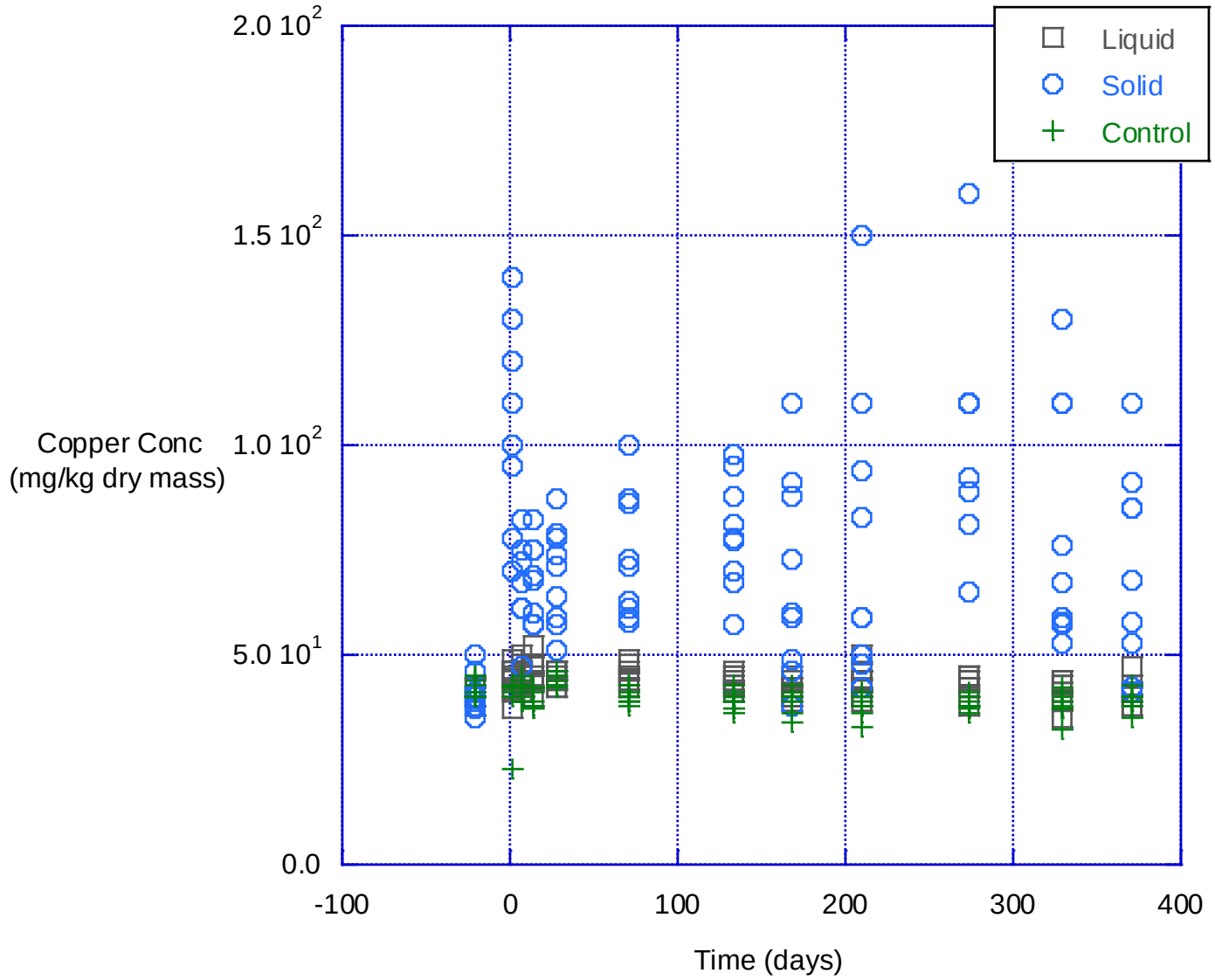
- Elevated in the solids and liquid treatments after application
- By day 120 near control levels



Copper Data

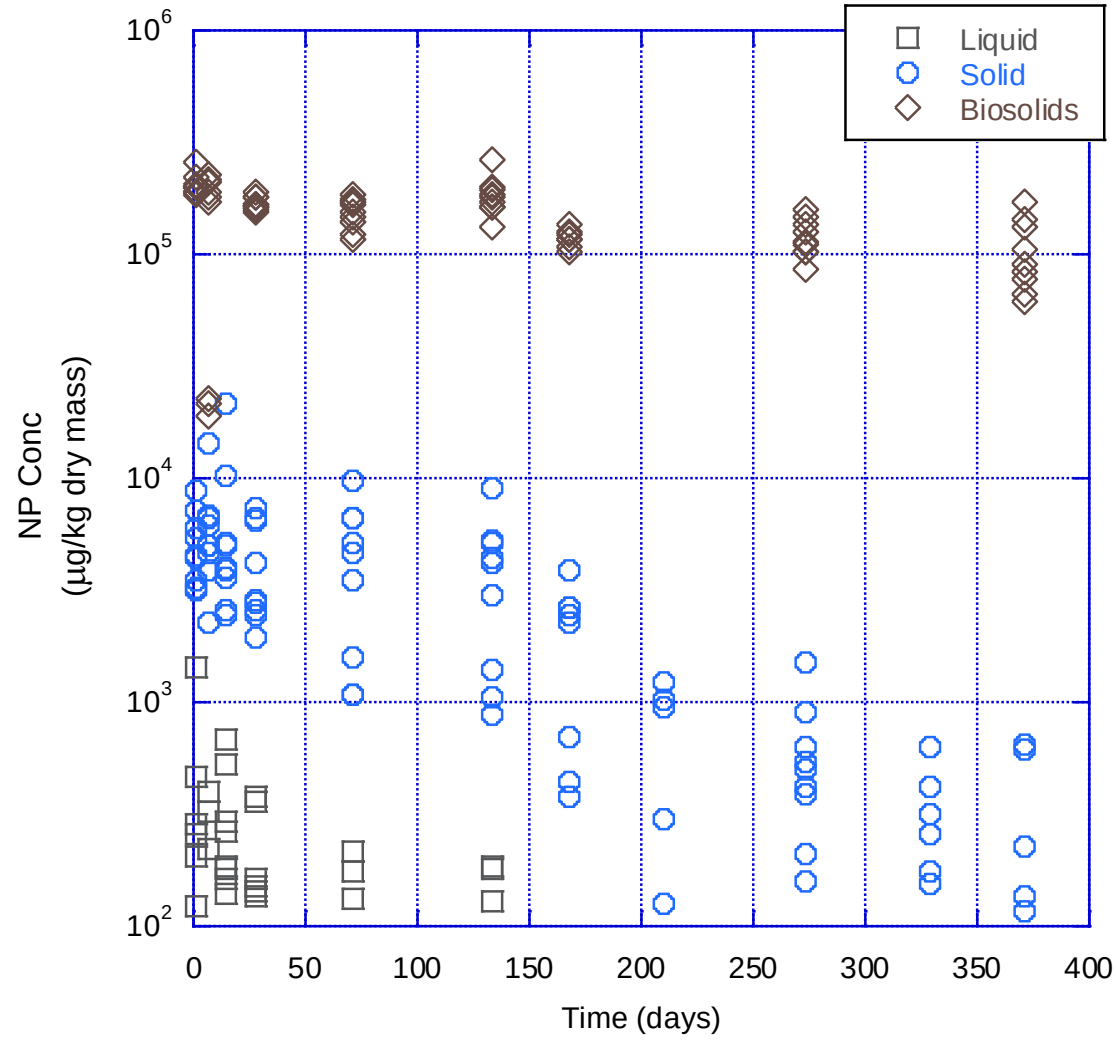
Concentrations

- Higher in the solid treatment throughout the study
- Liquid and control similar



Nonylphenol (NP) Data

- Aerobically degradable surfactant, weakly estrogenic
- Only concentrations above the reporting limit (RL) are shown
- RL ~ 120 µg/kg dry mass
- Liquid – no data > RL after 120 days
- NP persists in solid and biosolids throughout the study
- 34 % of samples did not meet QA acceptance criteria



PFAS by ASTM D7968 (LC/MS/MS)

- Matrix - Environmental solids such as soils, sediments, and sludges
  - Developed by Larry Zintek (Reg 5 Chicago Regional Laboratory)
  - Single lab validated

- Method
  - Solvent extraction
  - Analysis by LC/MS/MS with MRMs and ion ratios

- Target Analytes:
  - 11 Perfluorinated Carboxylic Acids (PFCAs): C4 - C14
  - 3 Perfluorinated Sulfonic Acids (PFSAs): C4-C10
  - Precursors
    - 6 PFCAs - 6:2, 8:2, 10:2, & 7:3 FTCA; and 6:2 & 8:2 FTUCA

- Surrogate standards (isotopically labeled compounds): 9 PFCAs and PFSAs
  - Used to monitor analytical method performance/quality
  - Not used to “correct” the data

LC/MS/MS Analytical Method – ASTM D7968

2 g sample

Surrogate

10 mL Methanol

Mix

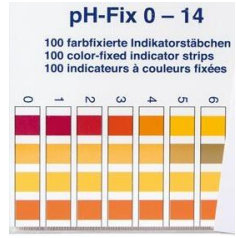
20 µL NH_4OH

Tumble 1 hr

Filter

10 µL Acetic Acid

Mix



Check pH

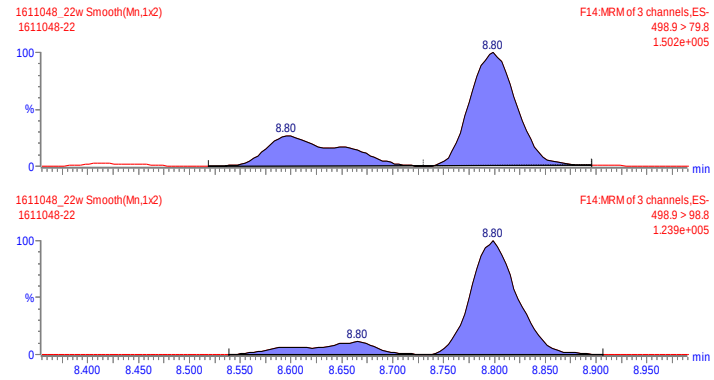
Transfer 1 mL sample in vial (pour)

Run time 21 min

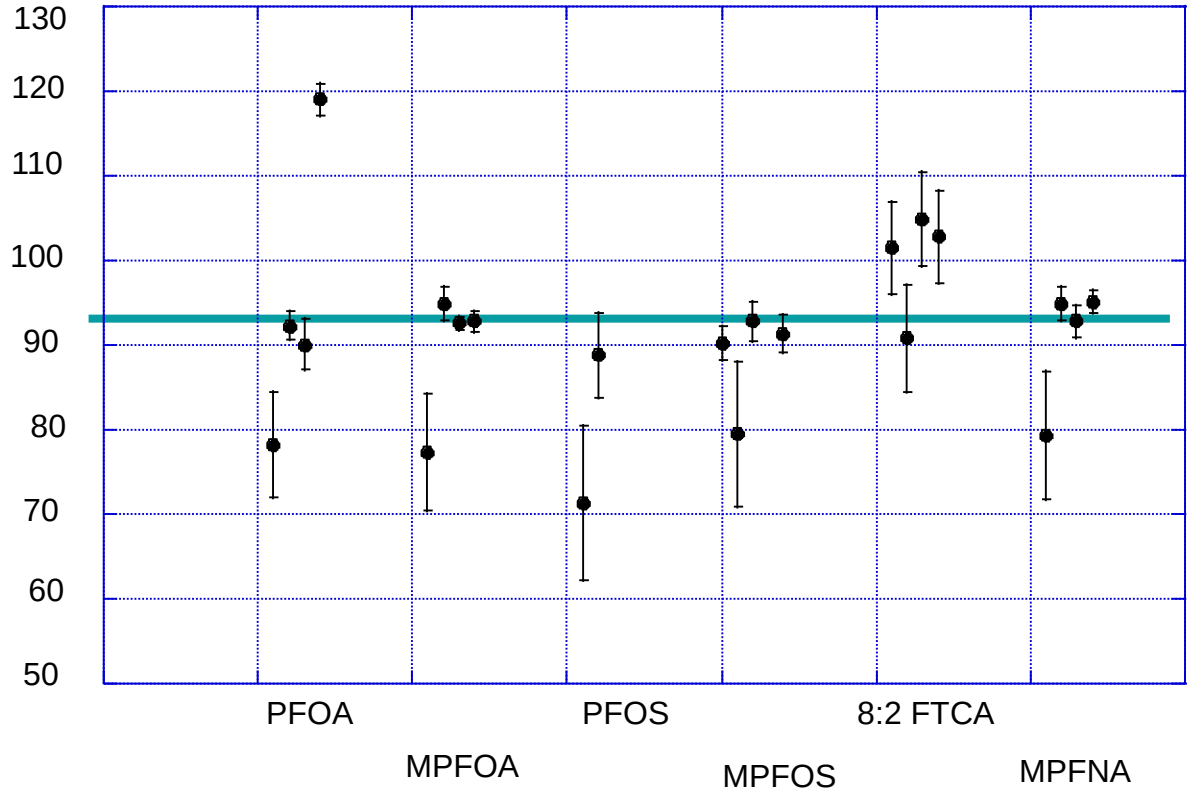
Based on schematic by William Lipps, Shimadzu

Analytical Method Quality Controls

- Analyte Identification
  - Each batch: Initial calibration, Calibration check, and Second source check
  - Each analyte: Retention time, Primary and Confirmation ion masses, and Ion ratio
- Accuracy – 2 of each per batch unless specified
  - Surrogate spiking - All samples and blanks
    - Used to assess method performance
    - Not used to alter reported concentrations
  - Matrix spike samples – MS and MS duplicates
  - Spiked blanks
  - Method reporting limit checks
- Precision - 2 of each per batch
  - Duplicate samples
  - Matrix spike duplicates
  - Spiked blanks
- Laboratory Contamination – method blanks – 2 per batch



ASTM D7968 Performance Data

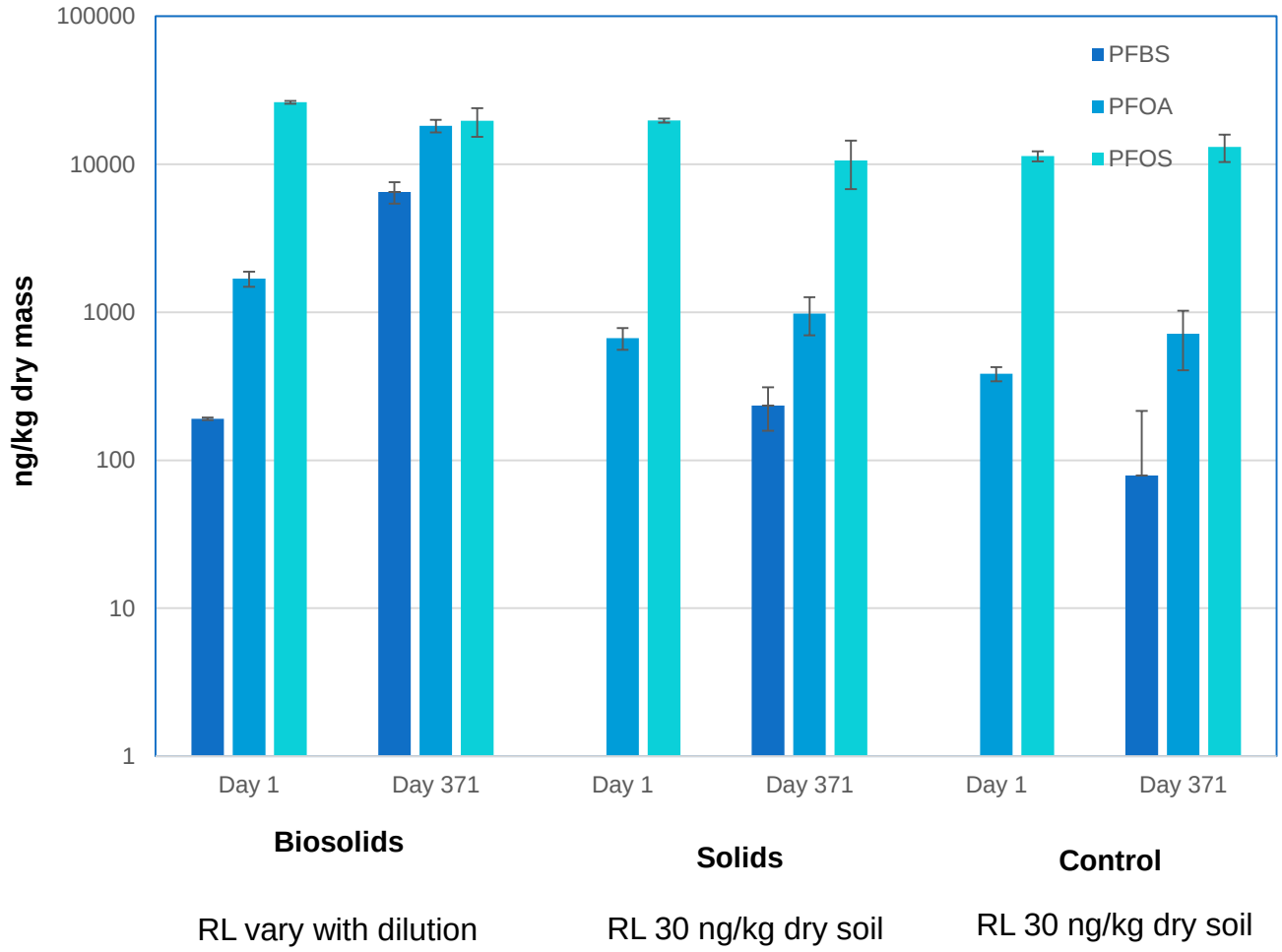


- Error bars are % RSD
- 6 replicates of each matrix
- Spiked at 400 ng/kg dry soil for all except 8:2 FTCA 8000 ng/kg dry soils
- 4 ASTM soil matrices: CL-1; CH-1; SP-1; ML-16

* PFOS not shown for SP-1 and ML-1 because the matrices had background conc comparable to spike conc

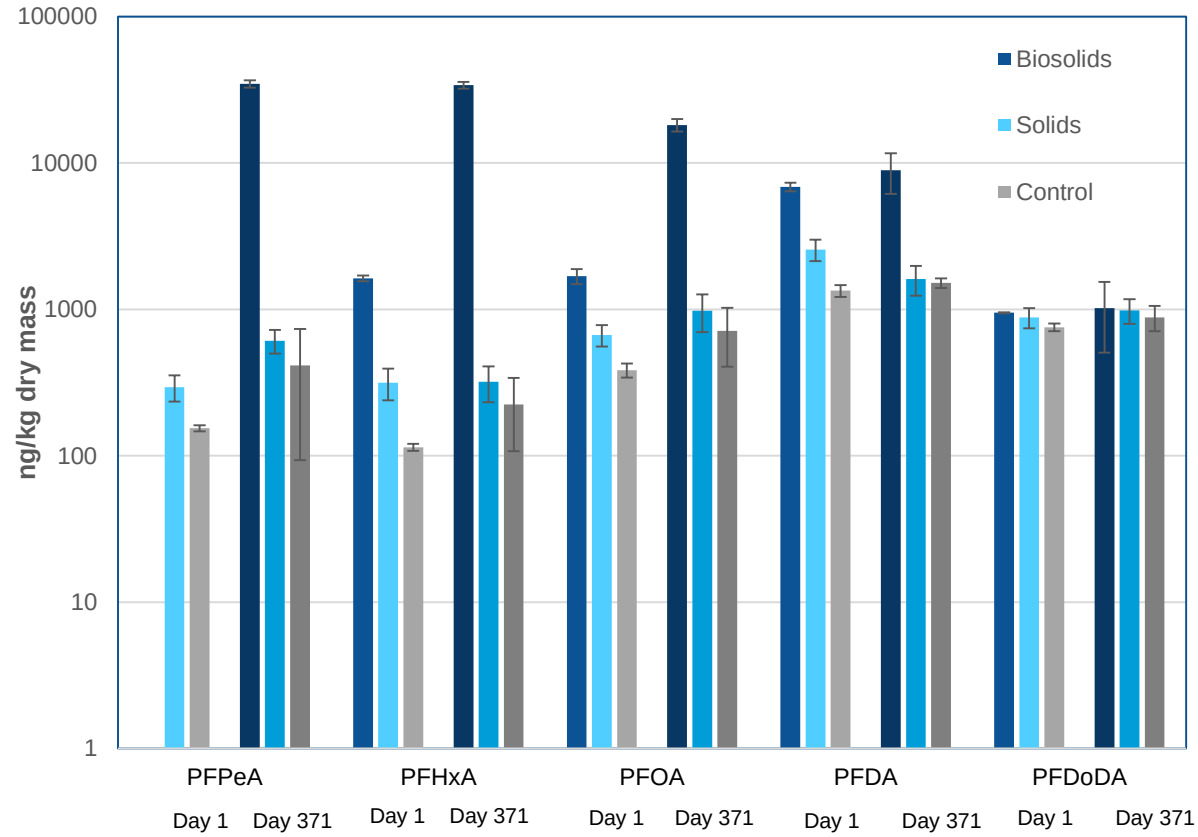
PFAS with EPA Screening Levels

- Conc above RL are shown
- Control soils have PFAS
- Conc increase with time for PFBS and PFOA in all trmts
- Superfund screening levels
  - PFBS 1600 mg/kg dry soil
  - PFOA 1.26 mg/kg dry soil
  - PFOS 1.26 mg/kg dry soil
- Some samples did not meet QA acceptance criteria
  - Biosolids controls 56 %
  - Solids application 23%
  - Control soil 8 %

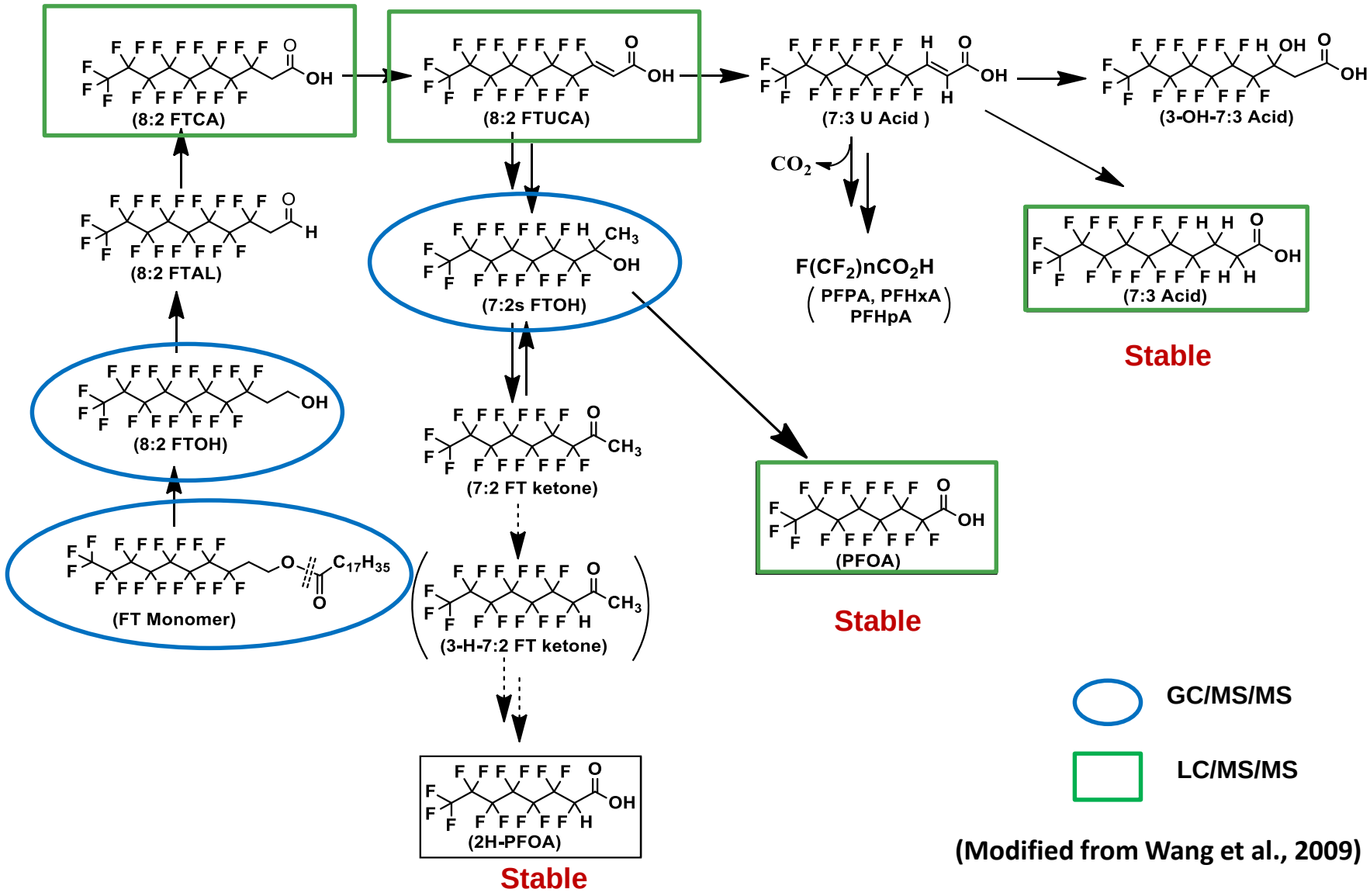


Other Observed PFAS

- Conc above RL are shown
  - Solids and control 30 ng/kg
  - Biosolids vary
- Biosolids show increasing conc with time
  - PFPeA
  - PFHxA
  - PFOA
- Solids show increasing conc with time
  - PFPeA
  - PFOA
- Control
  - Similar levels over time
  - Often similar to solids



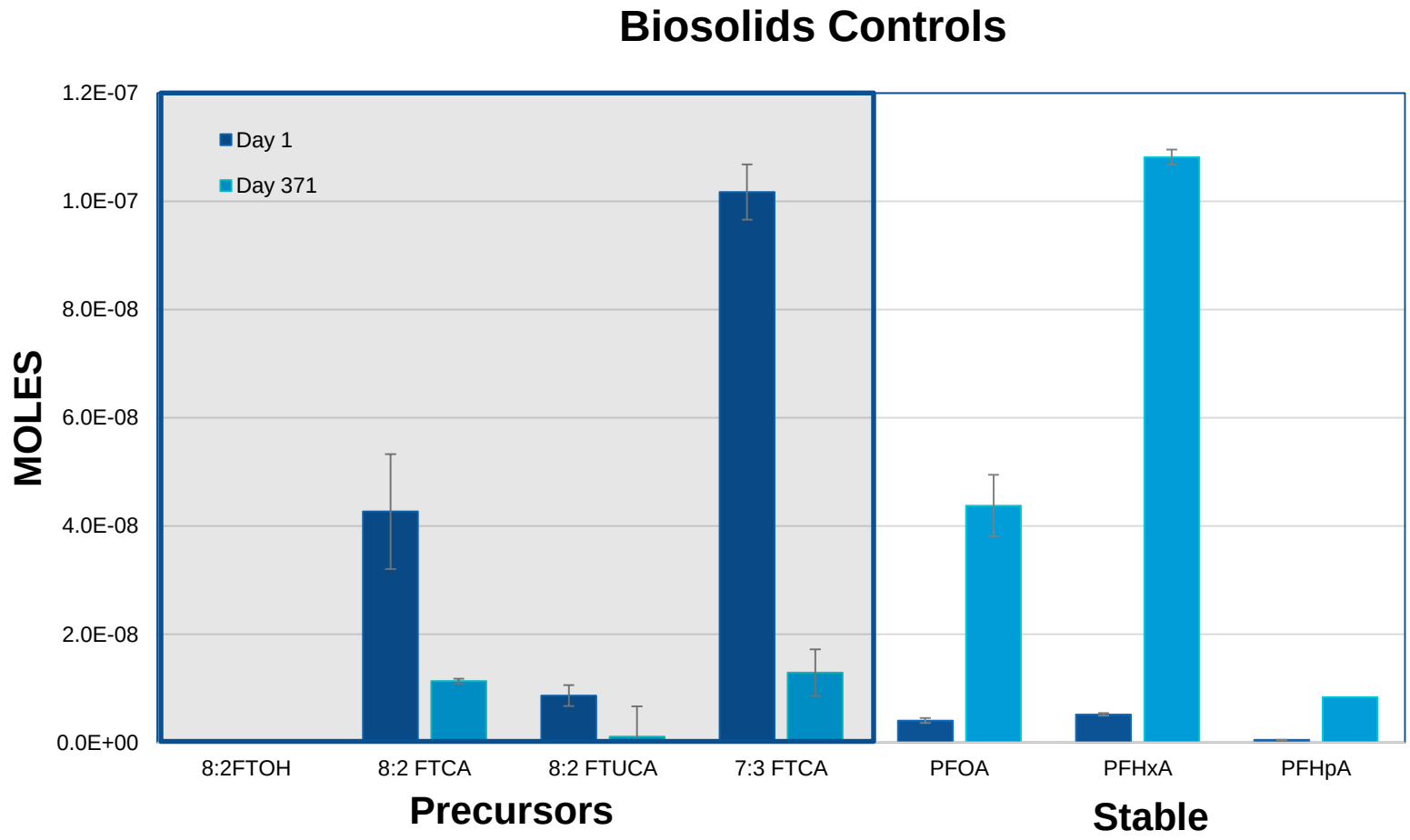
Oxidative Transformation to form PFOA



(Modified from Wang et al., 2009)

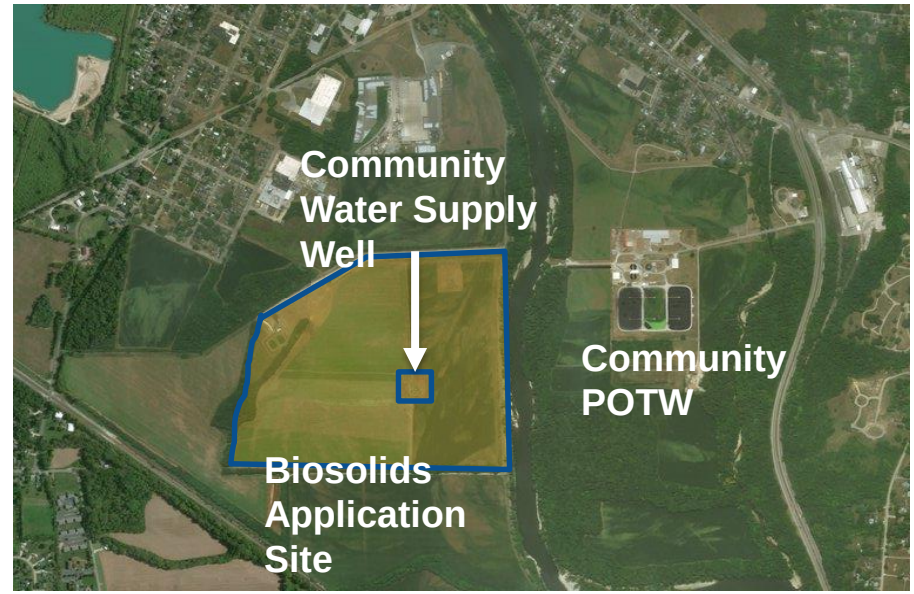
PFAS Transformation Products

- Precursor conc range similar to PFAA conc
- Precursor conc decrease with time
- Stable PFAAs increased
- 85% mole balance



Next Steps

- Complete data interpretation for study II
- Future Research
  - Characterize fate of precursors and transformation products
  - Characterize transport into vadose zone paired with ground water concentrations
  - Plan to use field and column studies



Conclusions

- Metals
  - Sodium at background levels in 120 days
  - Copper conc in solids > control and liquids throughout the study
- NP
  - Liquids - removed after 120 days
  - Solids
    - Consistent with previous study, little change in conc for 1st 100 days
    - Slow decline throughout the study
  - Biosolids conc similar throughout the study
- PFAS
  - Observed in all samples
  - Lower Molecular Weight (MW) conc > higher MW conc
  - Precursors present and appear to convert to stable end products

Acknowledgements

- Region 5 CRL: Francis Awanya, Anna Knoebel, Nidia Fuentes, Robert Thompson, Rob Snyder, Sylvia Griffin, Dennis Wesolowski, George Schupp
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- Others: Kavitha Dasu (currently Battelle Memorial Institute), Lawrence Wong (Senior Environmental Employee, CRL), Katrin Friesen (University of Alabama)

Acronyms

- PFAS- per- and polyfluorinated alkyl substances
- PFCAs- perfluorinated carboxylic acids
- PFSAs- perfluorinated sulfonic acids
- PFHxA- perfluorohexanoic acid
- PFOA- perfluorooctanoic acid (MPFOA- isotopic version)
- PFOS- perfluorooctane sulfonic acid (MPFOS- isotopic version)
- PFHpA- perfluoroheptanoic acid
- PFPeA- perfluoropentanoic acid
- PFBS- perfluorobutane sulfonic acid
- PFHpS- perfluoroheptane sulfonic acid
- FTUCA- fluorotelomer unsaturated acid (8:2 measured)
- FTCA- fluorotelomer saturated acid (6:2, 8:2, 7:3 and 10:2 measured)
- RL – Reporting Limit
- WWTP- wastewater treatment plant
- MRM- multiple reaction monitoring
- RSD- relative standard deviation
- PFNA- perfluorononionic acid (MPFNA- isotopic version)
- QA- quality assurance
- PFDA- perfluorodecanoic acid
- PFDoDA- perfluorododecanoic acid
- LC/MS/MS- liquid mass spectrometry
- GC/MS/MS- gas mass spectrometry
- PFAA- perfluorinated alkyl acid
- FTOH- fluorotelomer alcohol
- POTW- publicly owned treatment works
- MW- molecular weight

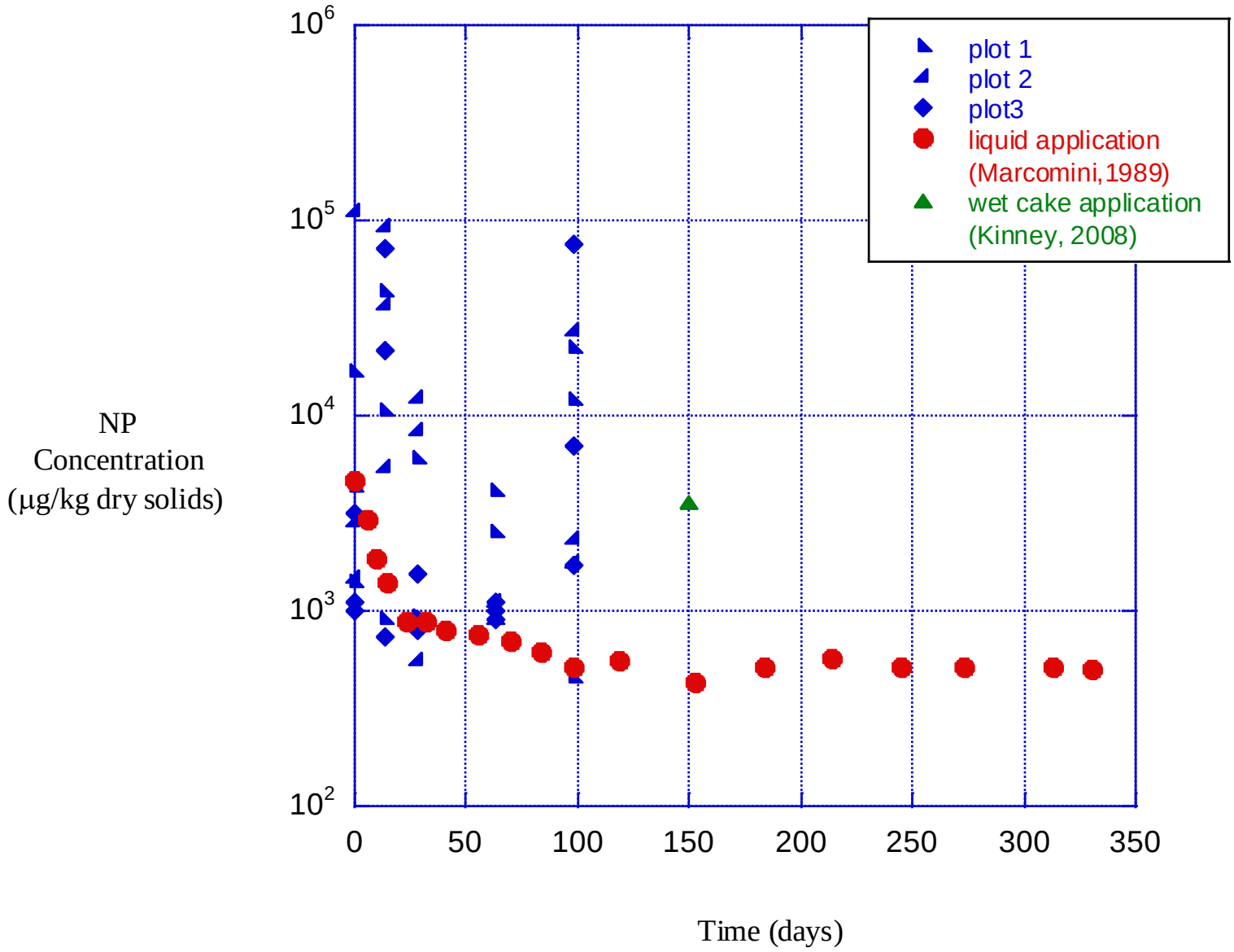
Treatment Plots - November

Liquid

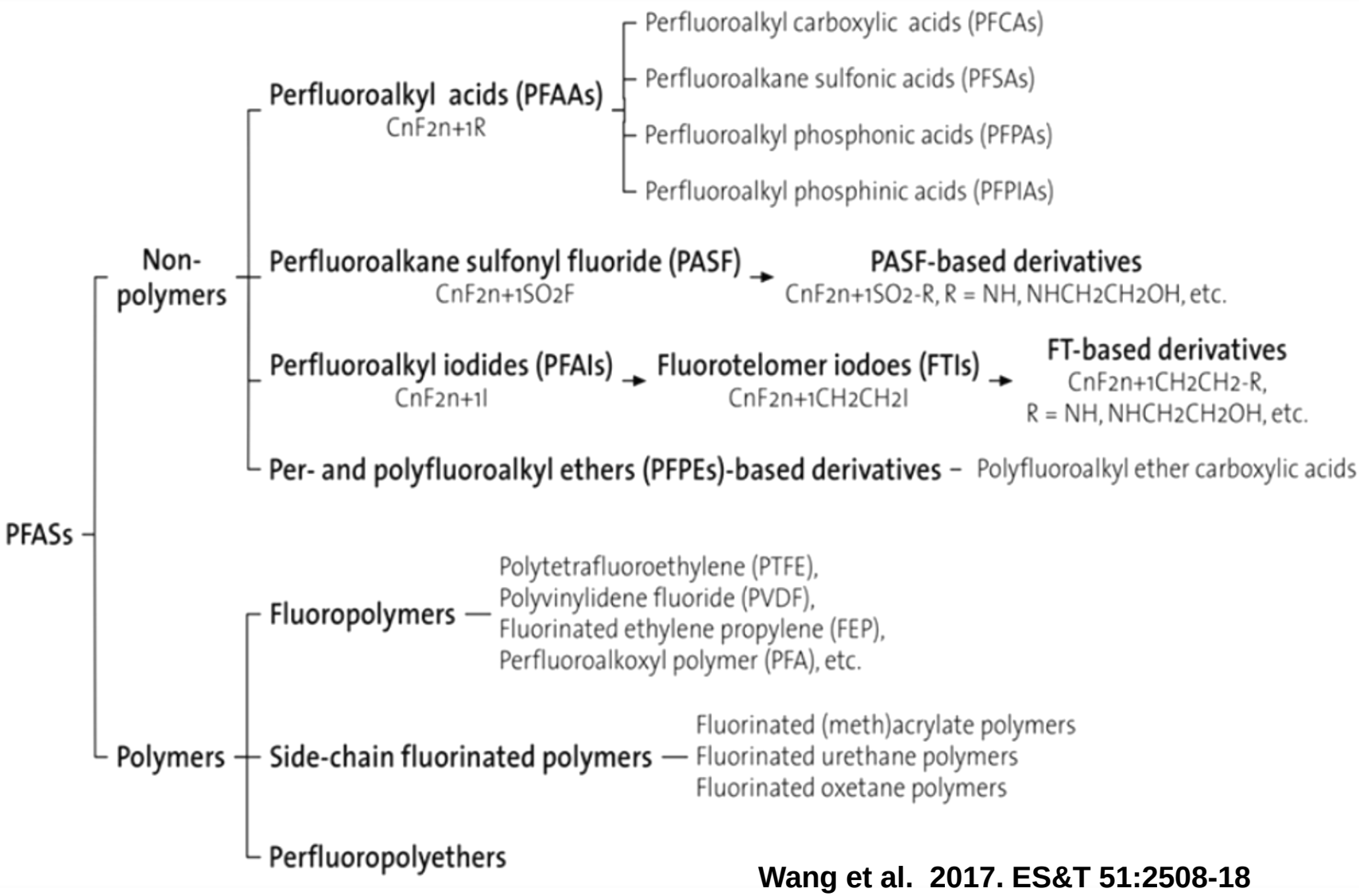
Solid

Control

Field Study I NP results



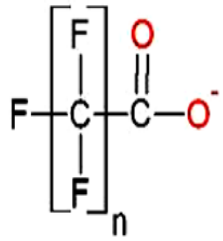
PFAS – More than just PFOA and PFOS



Wang et al. 2017. ES&T 51:2508-18

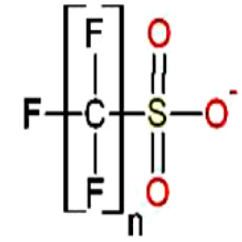
PFAS analytes

Perfluoroalkyl Carboxylates



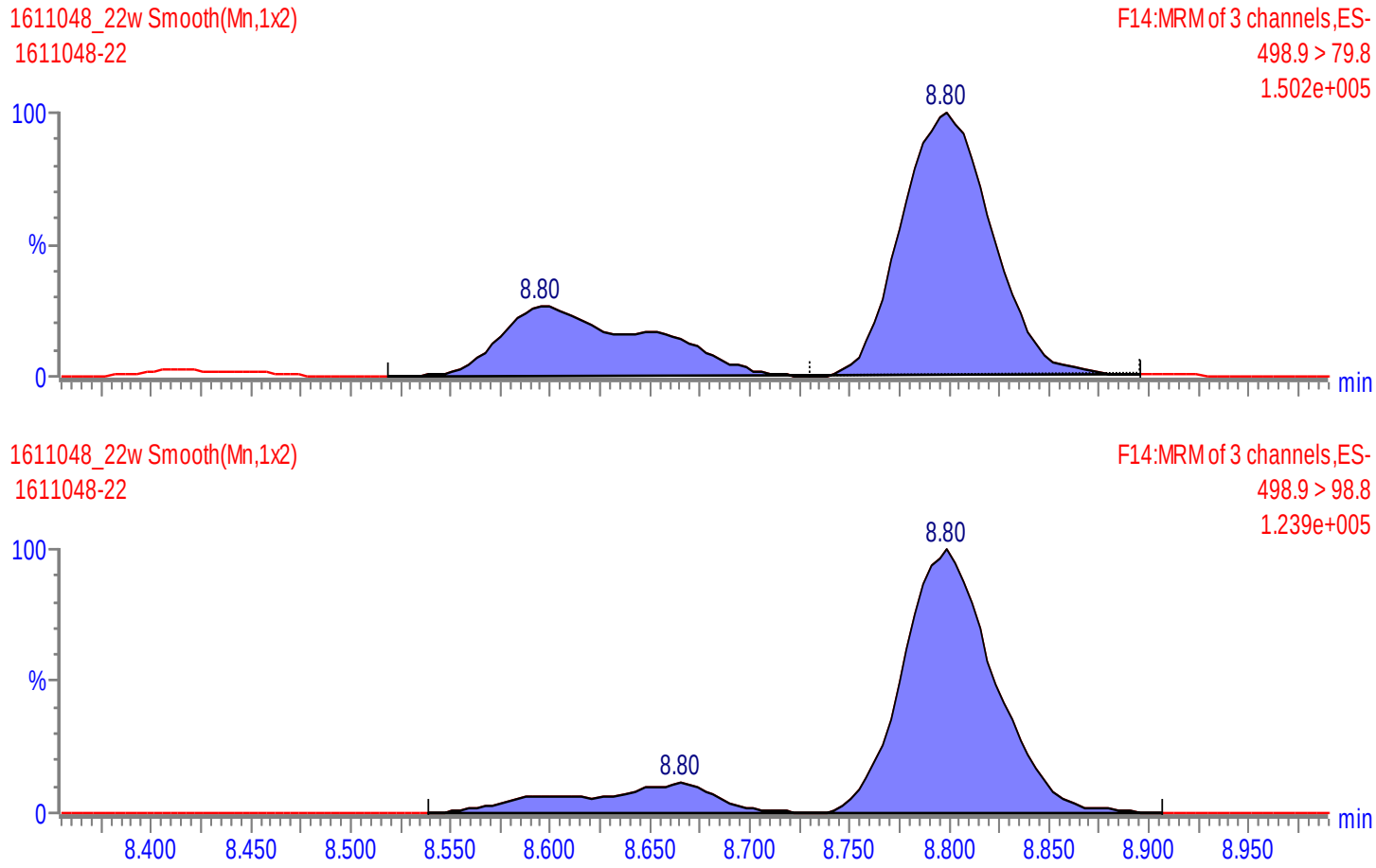
PFBA	n = 4
PFPeA	n = 5
PFHxA	n = 6
PFHpA	n = 7
PFOA	n = 8
PFNA	n = 9
PFDA	n = 10
PFUdA	n = 11
PFDoA	n = 12
PFTrA	n = 13
PFTeA	n = 14

Perfluoroalkyl Sulfonates



PFBS	n = 4
PFPeS *	n = 5
PFHxS	n = 6
PFHpS	n = 7
PFOS	n = 8
PFNS *	n = 9
PFDS	n = 10

Backe et al. 2013 ES&T


1611048_22w Smooth(Mn,1x2)
1611048-22
F14:MRM of 3 channels,ES-
498.9 > 79.8
1.502e+005
8.80
8.80
100
%
0
min
1611048_22w Smooth(Mn,1x2)
1611048-22
F14:MRM of 3 channels,ES-
498.9 > 98.8
1.239e+005
8.80
8.80
100
%
0
min
8.400
8.450
8.500
8.550
8.600
8.650
8.700
8.750
8.800
8.850
8.900
8.950

PFAS Sampling

- PFAS found in many common lab and field supplies and equipment
  - Teflon - equipment, seals, sample caps, and bottles
  - Water proof paper and PPE
  - Personal care products
  - Clothing – water and stain repellent fabrics
  - Surface treatment on aluminum foil, food wrappers
  - Blue Ice
  - Supplies – sharpies, post-it notes

- Avoid using these items when possible and pre-screen supplies and equipment
  - Claims of PFOS/PFOA free may contain C6 versions
  - Read labels and product descriptions carefully

- Information is evolving – check for updates
- Be careful about reusing existing equipment because of cross contamination – Decon and check for contamination

Equipment and supplies

Avoid:

- **Teflon, PTFE, and Fluoropolymers**
- **Aluminum foil may have PFAS surface treatment**
- **Decon 90, sharpies, post-it notes, waterproof papers or books**
- **Blue Ice**
- **Coated tyvek**

Acceptable

- **HDPE, polypropylene, and silicone materials**
- **Alconox or Liquinox**
- **Ball point pens**
- **Water ice – double bag in polyethylene bags**
- **Uncoated Tyvek (if necessary)**
- **Sample bottles follow analytical SOP (usually PP or HDPE, not glass)**

Other precautions

- Food packaging may contain PFAS treatments – careful where you eat and wash hands before returning
- Frequent nitrile glove changes
- Collect sample, field, and equipment blanks
- Spiked blanks used by some

Best practice

- Pretest materials and products for PFAS contamination
- Keep separate from “normal” supplies
- Test periodically for cross contamination